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THE REDUCING EFFECT OF ARGON IN THE PLASMA TREATMENT OF HIGH-MELTING NONMETALLIC MATERIALS (A REVIEW)

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The results of studying the plasma treatment of nickel (II) oxide and silicate glass are considered. It is demonstrated that argon plasma has weakly reducing properties.

Plasma processes in material treatment, synthesis of minerals, and development of technical and decorative coatings are generating special interest. This interest arises from a number of advantages over traditional technologies. They primarily include environmental cleanliness and substantial intensification of the process, a significant shortening of the production cycle, and the possibility of creating materials with a unique set of properties.

The studies by N. N. Rykalin, L. D. Svirskii, L. D. Kudinov, F. B. Vurzel', L. S. Polak, and other authors are dedicated to the use of low-temperature plasma in different technologies. Research in this field is carried out in the USA, Japan, Great Britain, Germany, and France.

Various sectors of industry use virtually the same type of plasma gun, whose operating principle is based on the use of an electric arc stabilized by concentric blowing with plasma-forming gases. The operating principle of this type of plasma gun involving gas stabilization of an electric arc is based on using direct and sometimes alternating current to transform the electric arc into a thermal arc.

Plasma heating based on the transformation of high-frequency energy, considering the relatively low power and low efficiency of high-frequency generators, is restricted to use in laboratory studies where low efficiency is not important. The only advantage of high-frequency plasma gun is its ability to operate in any atmosphere without electrodes. The absence of electrodes preserves the purity of the atmosphere used as the plasma-forming gas and does not contaminate the material [1].

The use of plasma-forming gases in electric-arc plasma guns is restricted due to the erosion of the cathode and the anode of the plasma burner. However, these drawbacks are compensated by the high efficiency of this type of plasma gun and the possibility of localization of thermal energy [2]. The application of a particular type of plasma gun is determined by the heating temperature, the degree of purity of the generating gas, the available power source, the arc power, and the efficiency of transformation of heat into gas energy.

Pure helium is rarely used in electric-arc plasma guns due to its short supply, high price, and high thermal conductivity. The latter property contributes to rapid heating and destruction of the electrodes. The use of hydrogen is possible only in treating oxide materials that are not reduced in this medium at the plasma flame temperature. Furthermore, hydrogen has high thermal conductivity and is explosion-prone. The plasma generated by nitrogen has high enthalpy; however, it applies a substantial thermal load to the electrodes, which leads to its rapid destruction. Argon is the most suitable gas with respect to its effect on the material [3]. Considering the high resistance of electrodes in argon plasma, the safety requirements, the relatively low cost of this gas, and the stability of materials spray-deposited in its flame, argon is currently one of the most common plasma-forming gases.

Nitrogen in the course of plasma treatment can enter into chemical reactions with materials and modify their structure and properties. Thus, in spray deposition of metallic titanium in nitrogen plasma, titanium nitride was discovered in the product [2]. In the course of treatment of spinel in nitrogen plasma, the formation of Mg_3Al_2 was registered [4]. The use of a mixture of nitrogen with hydrogen as plasma-forming

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gases in plasma spraying of hafnium carbide leads to the formation of hafnium carbonitride Hf(C, N), hafnium dioxide, and metallic hafnium. When argon and hydrogen were replaced by argon, nitrides were not formed, and other chemical compounds were not identified [5].

In the course of plasma spraying of niobium carbide in air, the oxygen content in the coating increases from 0.46 to 5.60% [6]. The oxygen content in the controlled argon atmosphere decreases compared to the initial value from 0.46 to 0.31%. It is suggested that the relative decrease in the oxygen content in the coating material occurs as a result of the reaction with carbon and emission of gaseous reaction products CO and CO_2 [6].

The high plasma temperatures make it possible to produce aluminum from kaolin. Thus, kaolin mixed with charcoal was subjected to plasma treatment. The plasma-forming gas was a mixture of argon and nitrogen in the ratio of 1 : 1. The plasma temperature was about 18,000 K. As a result of plasma treatment, the following products were formed: Al, AlN, Al_4C_3, Si, SiO, and SiC [7].

Argon under normal conditions has clearly expressed neutral properties. Plasma is the fourth state of the matter, for which the classical laws of thermodynamics are not effective. A vast practical database shows that it is impossible to predict the rate of reactions only on the basis of thermodynamic calculations. A great number of particles having high chemical activity are formed in the plasma flame, which cause additional chemical processes. Such activated particles include ionized atoms of plasma-forming gases [8].

Argon in its plasma state can have weakly reducing properties. This fact can be indirectly confirmed by studying the thermal decomposition of materials in argon plasma for the purpose of obtaining materials of various degrees of purity [9 – 11] (Table 1).

In spite of the wide use of plasma technologies in melting, cutting, and treatment of metals and in the production of alloys and intermetallic compounds, the studies of the effect of plasma processes on high-melting metallic materials are sporadic and non-systematic. The subject of the plasma synthesis of minerals, in particular, magnesia spinel, yttrium-aluminum garnet, and amethyst, is in the initial stage of research [12 – 14].

Several studies [15 – 17] are dedicated to decorative plasma treatment of ceramics in order to obtain a glaze layer of their surface. The authors in their studies concentrated on the optimization of the process parameters and treatment conditions. The effect of argon plasma on the properties of the glaze layer formed on the surface of ceramics was actually not considered.

The purpose of the present study is to investigate the specifics of the reducing effect of argon used as a plasma-forming gas. This problem is topical, since its solution will make it possible to develop and scientifically substantiate the technologies for plasma synthesis of minerals and the methods for producing oxide coatings of special and decorative destination for ceramic and glass surfaces with a set of prescribed properties.

TABLE 1

Material	Thermal decomposition products	Weight content of resulting compounds, %	Reference
$Fe(CO)_5$	C	1.0	[9]
	C (fixed)	2.3	
	Fe	60.0	
Molybdenum ore (concentrate)	Mo	99.8	[10]
BF_3	B	94.8	[11]
BCl_3	B	99.1	[11]

Nickel(II) oxide was chosen for studying the reducing effect of argon plasma on oxides. Preliminarily molded and fired nickel(II) oxide rods were inserted in the GN-5r plasma burner of the UPU plasma gun and spray-deposited on the metal substrate of grade St.3 steel. The operating parameters of the plasma gun were as follows: working voltage 30 V, current 450 A. The plasma-forming gas was argon and its flow rate was 0.0114 g/sec at the pressure 0.24 MPa.

The phase composition of NiO subjected to plasma treatment was identified by x-ray phase analysis, petrography, spectral and chemical methods, as well as electron microscopy.

It was determined by preliminary thermodynamic calculations that at a temperature above 2187°C, the equilibrium of the system $2Ni + O_2 = 2NiO$ is shifted toward the initial compounds.

The objects of study were spheroids 200 – 325 μm in diameter. They were found to have weak magnetic properties. A study of a sample fracture with a microscope in obliquely reflected light revealed the existence of sites with strong metallic luster. For further identification of metallic nickel, the spheroids were studied in reflected light using preliminarily pickled oblique polished sections. This made it possible to identify finely disperse formations and aggregate conglomerations with a strong reflecting capacity typical of elemental nickel.

X-ray phase analysis corroborated the presence of metallic nickel by identifying diffraction maxima with interplanar distances $d = 2.03$, 1.76, and 1.24 Å. A certain expansion of the lines of the main diffraction maxima ($d = 2.41$, 2.08, 1.48, 1.26, 1.21, 1.18, and 1.05 Å) indicated the deficit of oxygen in the crystalline lattice of nickel(II). The electron-graphic analysis as well confirmed the existence of metallic nickel in NiO spheroids after plasma treatment.

For a further study of the reducing effect of argon plasma, a composite material was selected, i.e., nickel(II) oxide with soda-lime glass in the ratio 20 : 80. The glass composition was as follows (wt.%): 67.80 SiO_2, 2.65 Al_2O_3, 0.25 CaO, 6.80 CaF, 19.60 Na_2O, 1.10 K_2O, and 1.80 B_2O_3. The components were premixed in a ball mill and then mixed

with a binder represented by flour glue or PVA glue molded in the shape of rods. The molded rods were dried and fired.

Before plasma treatment the rods were fired in the charge at a temperature of 1260°C. Nickel(II) oxide in firing reacted with silicon oxide of the glass. As a result, nickel orthosilicate Ni_2SiO_4 was formed, which was corroborated by x-ray phase analysis (the identified diffraction maxima with interplanar distances $d = 4.28$, 3.72, 3.44, 2.74, 2.48, and 2.22 Å).

Nickel orthosilicate under plasma treatment completely decomposed, and the coating material exhibited metallic nickel, nickel(II) oxide, and an amorphous vitreous phase based on glass. The petrographic studies as well substantiated the existence of nickel(II) oxide and elemental nickel in the initial material subjected to plasma treatment. Nickel orthosilicate was identified on the basis of the optical constants $n_g = 1.928 \pm 0.003$ and $n_p = 1.872 \pm 0.003$, and nickel (II) oxide was identified on the basis of $n_o = 2.36 \pm 0.01$.

Thus, the performed study shows the weakly reducing effect of argon in the plasma treatment of high-melting nonmetallic materials. These specifics of the effect of argon plasma on the reducing processes have to be taken into account in the synthesis of minerals and in the production of protective and decorative coatings.

REFERENCES

1. V. I. Dembrovskii, *Plasma Metallurgy* [in Russian], Metallurgiya, Moscow (1981).
2. L. N. Usov and A. I. Borisenko, *Use of Plasma for Producing High-Temperature Coatings* [in Russian], Nauka, Moscow – Leningrad (1965).
3. W. Grafe, M. Blank, and F. Winsman, “Ione naustanchan glas mittels plasma trahlen,” *Silikattechn.*, No. 5, 132 – 133 (1981).
4. L. D. Svirskii and Yu. A. Pirogov, “A study of the properties of heat-resistant coatings on metal,” *Steklo Keram.*, No. 9, 31 – 35 (1964).
5. M. N. Levinstein, A. Eisenlohr, and B. E. Kramer, “Properties of Plasma-Sprayed Materials,” *Welding J.*, **40**(1), 5 – 8 (1961).
6. V. S. Blokhin, S. V. Mel’nikov, and G. P. Telegin, “Decoding of the phase composition of plasma-sprayed coatings based on niobium carbide using micro-x-ray and microstructural color analysis,” in: *Inorganic and Organosilicate Coatings* [in Russian], Nauka, Leningrad (1975), pp. 122 – 128.
7. D. Novotny, “Desilikace kaolinu v plasmaru,” in: *V Vedeska Konf. VSB*, Ostrava (1971), p. 100.
8. V. S. Blokhin, V. G. Saksel’tsev, and S. V. Mel’nikov, “A study of the behavior of niobium carbide in a low-temperature plasma jet and the properties of the formed coatings,” in: *Inorganic and Organosilicate Coatings* [in Russian], Nauka, Leningrad (1975), pp. 128 – 132.
9. O. V. Sitnikov, “The final stage of reduction of oxidized iron in plasma-arc remelting,” in: *Proceed. of 5 All-Union Conf. “Plasma Processes in Metallurgy of Inorganic Materials”* [in Russian], Moscow (1980), p. 120.
10. P. Huska and C. Clump, “Decomposition of Molybdenum Disulfide in an Induction-Coupled Argon Plasma,” in: *Ind. Eng. Chem. Proc. Desing Develop.* (1967), p. 6.
11. H. Schoumaker, “Foura plasma triphase,” in: *Publication Electrotherm Communication an C.B.B.E.* (1971), p. 36.
12. V. P. Krokhin, V. S. Bessmertnyi, O. V. Puchka, and O. N. Shvyrkina, ”Synthesis of yttrium-aluminum garnet,” *Steklo Keram.*, No. 5, 18 – 19 (1998).
13. V. P. Krokhin, V. S. Bessmertnyi, O. V. Puchka, and A. D. Kirienko, “The role of the modifying chromium ion in the structure of magnesium spinel,” *Steklo Keram.*, No. 9, 13 – 16 (1998).
14. V. S. Bessmertnyi, O. N. Shvyrkina, and P. S. Dyumina, “On the synthesis of synthetic amethyst,” in: *Proceed. of Scient.-Pract. Conf. of Teachers and Researchers of BKAPK* [in Russian], Belgorod (1995), pp. 167 – 173.
15. N. N. Dolgopolov, “Prospects of using plasma technology in the production of construction materials,” *Stroit. Mater.*, No. 1, 10 (1975).
16. M. E. Ermolaev, V. K. Polyanskii, and M. P. Voronin, “Production of protective and decorative coatings employing a plasma gun,” *Stroit. Mater.*, No. 6, 21 – 22 (1976).
17. N. I. Lepnitskaya, V. B. Shimanovich, A. K. Shipai, and T. N. Osipova, “Certain specifics of the technology of facing bricks with fused surface,” in: *Intensification of Technology Processes in Production of Construction Materials and Improvement of Their Quality* [in Russian], Minsk (1974), pp. 104 – 108.